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Measurement of Actinides in Molybdenum-99 Solution

Analytical Procedure

November 2015

C. Soderquist
J. Weaver

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Summary

This document is a companion report to a previous report, PNNL 24519, *Measurement of Actinides in Molybdenum-99 Solution, A Brief Review of the Literature*, August 2015. In this companion report, we report a fast, accurate, newly developed analytical method for measurement of trace alpha emitting actinide elements in commercial high-activity molybdenum-99 solution. Molybdenum-99 is widely used to produce ^{99m}Tc for medical imaging. Because it is used as a radiopharmaceutical, its purity must be proven to be extremely high, particularly for the alpha emitting actinides.

This analytical method assumes that the required purity is less than one part alpha emitters in 10^9 parts ^{99}Mo (by activity). The activity of the commercial ^{99}Mo solution is assumed to be 10 mCi per mL. The chemical composition of the commercial ^{99}Mo solution is assumed to be about 0.010 M sodium molybdate (a carrier for ^{99}Mo) in 0.2M sodium hydroxide solution (high pH conditions to maintain the molybdenum in the chemical form MoO_4^{2-}) with a low concentration of sodium nitrate (0.010M, from chemical processing).

The high beta-gamma activity of the ^{99}Mo solution complicates the measurement of alpha emitters. The high activity and the dissolved sodium hydroxide preclude direct measurement of alpha emitters by alpha spectrometry. The high dose rate requires special equipment and shielding to avoid excessive exposure to the laboratory analyst. In this new analytical method, the alpha emitting actinides are separated from the high activity ^{99}Mo and ^{99m}Tc by simple coprecipitation on 50 μg of gadolinium carrier from dilute ammonium hydroxide. Only simple equipment is required, and the high activity parent sample does not need to be handled directly.

The sample of ^{99}Mo solution is measured into a vessel (such as a polyethylene centrifuge tube) and acidified with dilute nitric acid. A gadolinium carrier is added (50 μg). Tracers and spikes are added as necessary. Then the solution is made strongly basic with ammonium hydroxide, which causes the gadolinium carrier to precipitate as hydrous $\text{Gd}(\text{OH})_3$. The precipitate of $\text{Gd}(\text{OH})_3$ carries all of the actinide elements. The suspension of gadolinium hydroxide is then passed through a membrane filter to make a counting mount suitable for direct alpha spectrometry. The high activity ^{99}Mo and ^{99m}Tc pass through the membrane filter and are separated from the alpha emitters. The gadolinium hydroxide, carrying any trace actinide elements that might be present in the sample, forms a thin, uniform cake on the surface of the membrane filter. The filter cake is first washed with dilute ammonium hydroxide to push the last traces of molybdate through, then with water. The filter is then mounted on a stainless steel counting disk. Finally, the alpha emitting actinide elements are measured by alpha spectrometry.

The precipitation can be repeated to increase decontamination from ^{99}Mo and ^{99m}Tc . The gadolinium hydroxide filter cake will dissolve readily in dilute nitric acid. As necessary, the gadolinium hydroxide precipitate can be dissolved, re-precipitated, and re-mounted in a clean membrane filter.

The alpha spectral resolution is sufficient to resolve ^{242}Pu from ^{239}Pu . Recovery has been shown to be essentially quantitative for uranium, neptunium, plutonium, and americium.

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1.0 Purpose, Scope, and Applicability

The purpose of this analytical method is to provide a fast, reliable measurement of alpha emitting actinide elements, particularly uranium, plutonium, and americium, in a high-activity ^{99}Mo solution. The ^{99}Mo solution is used commercially to produce $^{99\text{m}}\text{Tc}$ generators for medical imaging. This report summarizes the analytical method developed for this measurement in a high activity ^{99}Mo solution.

The target analytes are ^{235}U , ^{239}Pu , and ^{241}Am , although any other actinide alpha emitters will also appear in the alpha spectrum and can be measured. Molybdenum-99 has traditionally been made by irradiation of high enriched ^{235}U . Because of the threat of proliferation of weapons by diversion of highly enriched uranium, manufacturers have recently been encouraged to switch from high enriched ^{235}U (HEU) to 20% enriched ^{235}U (low enriched uranium, LEU), which is not suitable for weapons and is not a proliferation risk. The process for making ^{99}Mo is essentially the same for LEU as it is for HEU, but the LEU has 80% ^{238}U , which the HEU does not have. In a reactor, the ^{238}U picks up a neutron and ultimately forms ^{239}Pu . The product ^{99}Mo must be shown to be essentially free of ^{239}Pu . Because HEU has much less ^{238}U , it makes much less ^{239}Pu .

The ^{99}Mo is made by fission. A target made of LEU is placed in a reactor and allowed to fission long enough for a useful amount of ^{99}Mo to accumulate. After the LEU target has been irradiated in a reactor, the target is dissolved and chemically processed to recover the ^{99}Mo , free of other fission products and the actinide elements. This ^{99}Mo product is used to make $^{99\text{m}}\text{Tc}$ generators for medical diagnostics. The ^{99}Mo activity is in the range of tens of millicuries per mL. Alpha emitters must be shown to be essentially absent in the ^{99}Mo . This work assumes that the alpha activity must be less than the ^{99}Mo activity by a factor of 10^9 . Because of the extremely high beta-gamma activity of the ^{99}Mo solution, the alpha emitters must be separated before they can be measured. The separated alpha emitters can then be mounted for alpha spectrometry and measured.

For this analytical method, the ^{99}Mo solution is assumed to have an initial activity of about 10 mCi per mL. The ^{99}Mo solution is assumed to consist of 0.01M sodium molybdate (carrier from molybdenum separation), 0.01M sodium nitrate (from chemical processing), and 0.2M sodium hydroxide (to keep the pH high and maintain ^{99}Mo in solution as MoO_4^{2-}). Because the ^{99}Mo has a half-life of only 2.75 days, the alpha measurement must be fast, so that valuable product is not unnecessarily lost to decay. The actinide alpha activity must be proven to be less than the ^{99}Mo activity by a factor of 10^9 after some period of decay, at a particular reference time.

2.0 Detection Limit for Alpha Activity

The sample size and count length can be calculated from the upper limit on alpha contamination in the ^{99}Mo . If the ^{99}Mo is allowed to decay through two half-lives (5 days for analysis, manufacture of the generator, and shipping), then the ^{99}Mo activity will decay to 2.5 mCi/mL. The alpha activity must be less than this by 10^9 , or 2.5×10^{-9} mCi/mL. This is about 6 decays per minute per mL. If the measured alpha activity is less than 6 decays per minute per mL of ^{99}Mo solution after five days of decay, then the solution will meet the $<10^9$ criterion for alpha contamination. This calculation of detection limit assumes that the actinide yield through the chemistry is high.

The detection limit widely used in radiochemistry is the point where the result has a 5% chance of a false positive and, at the same time, a 5% chance of a false negative. See Lloyd A. Currie ¹. The reporting limit required by a radiopharmaceutical manufacturer will be the lowest concentration at which the analytical precision is some value, such as $\pm 15\%$ or $\pm 20\%$. The measured concentration of alpha emitter will probably be required to be below some reporting limit, even if it is above the formal detection limit.

The sample taken for alpha analysis should be as small as practical so that a minimal amount of valuable ⁹⁹Mo product is consumed and lost. The count length should be as short as possible so that the analysis is finished promptly. A longer count would permit a smaller sample size, but a bigger sample would allow a shorter count and faster results.

In a typical alpha spectrometry measurement the counting efficiency is around 0.2 counts per decay. A clean detector will have a background around 0.001 count per minute in the region of interest. (A new detector will probably have a background of zero in the same region, but the detector will slowly accumulate background activity as it is used. A more realistic case is a clean, but used detector with a small, non-zero background.) The following table shows the attained detection limit for various count lengths, assuming a 1 mL sample size and 80% chemical yield. The ⁹⁹Mo is assumed to have decayed through 2 half-lives, from 10 mCi/mL to 2.5 mCi/mL.

Molybdenum-99 activity	2.5	mCi/mL
Sample size	1	mL
Detector counting efficiency	0.2	counts per decay
Detector background in peak	0.001	counts per minute
Chemical yield of actinide separation	80%	
Max permissible alpha activity	2.5E-09	mCi/mL

Count length, minutes	Alpha detection limit, mCi/mL
100	1.2E-10
200	6.7E-11
500	3.4E-11
1000	2.1E-11

This shows the detection limit can be met with a count as short as 100 minutes using a 1-mL sample, but the data may still not meet the reporting limit precision criteria. The following table shows the calculated counting error for a range of alpha concentrations from just below to just above the specification limit for alpha contamination. The count length is assumed to be 100 minutes. Counting error will be the largest source of uncertainty and will heavily dominate the observed spread of the data. The specification limit for alpha contamination is 2.5E-09 mCi (second line in the table below).

Alpha activity, mCi	Peak area, counts	Counting error, % at 1s
3.00E-09	107	± 10%
2.50E-09	89	± 11%
2.00E-09	71	± 12%
1.50E-09	53	± 14%
1.00E-09	36	± 17%
5.00E-10	18	± 24%

Counting error at 1 standard deviation is the square root of the number of counts. The sample count and the background count are two independent, uncorrelated measurements and must be combined in quadrature, using simple algebra. Expressed as a percent, counting error is calculated as follows:

$$1s \text{ counting error} = \frac{\sqrt{\text{gross peak area} + \text{background peak area}}}{\text{net peak area}} \times 100$$

This calculation ignores the small contribution from the tracer peak.)

3.0 Description of the Chemistry

Alpha emitting contaminants in ^{99}Mo are separated from the sample by coprecipitation on 50 μg of gadolinium in ammonium hydroxide, then measured by alpha spectrometry. The raw sample is made slightly acidic with nitric acid, 50 μg of gadolinium is added, and then the sample is made strongly basic with ammonium hydroxide. Gadolinium hydroxide precipitates at the high pH and carries all of the actinides with it. Sodium ion, molybdate, nitrate, and pertechnetate are all soluble in strong ammonium hydroxide and remain in solution. The suspension of $\text{Gd}(\text{OH})_3$ in aqueous NH_4OH , with dissolved sodium salts, is passed through a membrane filter. The precipitate of $\text{Gd}(\text{OH})_3$ stops at the filter, but all of the dissolved species pass through, including the ^{99}Mo and $^{99\text{m}}\text{Tc}$. The thin layer of $\text{Gd}(\text{OH})_3$ on the membrane filter can be counted directly for alpha emitters on an alpha spectrometer.

A single precipitation may not reduce the ^{99}Mo activity sufficiently. The very small volume of $\text{Gd}(\text{OH})_3$ will not occlude much of the solution, but the ^{99}Mo activity is very high and even a tiny volume of occluded ^{99}Mo solution could have high activity. The precipitate can be dissolved off the filter with dilute nitric acid and collected, then re-precipitated as before and placed on a clean filter. The second precipitation will greatly reduce the ^{99}Mo beta-gamma activity.

The task is essentially the separation of the actinide elements (collectively) from 10 millimolar molybdate and trace level pertechnetate. Alpha emitters must first be separated from the sample; they cannot be measured directly in the ^{99}Mo solution. The high dissolved solids (from 0.2M NaOH) will

cause the sample to absorb its own alpha emission, and the beta-gamma activity would be too high to safely handle in the counting equipment. Also, the high beta-gamma activity would interfere with the alpha measurement.

All of the actinide elements have highly insoluble hydroxides and will coprecipitate on rare earth hydroxide carriers. Molybdate and pertechnetate are soluble simple anions (MoO_4^{2-} and TcO_4^-) in basic solution. The trace actinides will probably be present as uncharged hydrous oxides, or possibly anions in the strongly basic ^{99}Mo solution. Pertechnetate ion and the actinide elements will be present at trace concentration, too low to precipitate without a carrier. The analytical method presented here has been tested with uranium, neptunium, plutonium, and americium and has been found to give essentially quantitative recovery in a single precipitation. (Double precipitations will have lower recovery.) The other actinide elements also have highly insoluble hydroxides and would be expected to also show high recovery by coprecipitation on a rare earth hydroxide.

Since the actinides will be present at very low concentrations, perhaps not detectable, they probably would not interfere with each other in the alpha spectrum, and do not need to be separated from each other before counting.

Uranium, if present in the ^{99}Mo solution, will very likely be in the hexavalent oxidation state. Trivalent uranium is quickly oxidized to U(IV) by air, and U(IV) is slowly oxidized by air to U(VI). Plutonium could be present as Pu^{3+} , Pu^{4+} , PuO_2^+ , or PuO_2^{2+} (see J. M. Cleveland, *The Chemistry of Plutonium*, reference 2). Americium has only one stable oxidation state (except under extremely oxidizing conditions³ which will never exist in the ^{99}Mo solution), and can be present only as Am^{3+} . All of these species hydrolyze easily, particularly Pu^{4+} . In the ^{99}Mo solution, which is 0.2 molar sodium hydroxide, the actinides probably exist as uncharged hydroxides or as anions, but probably not as free cations. Commercial sodium hydroxide always has a few percent carbonate, which is a strong ligand for tetravalent and hexavalent uranium and plutonium. Uranium and plutonium, if present in the ^{99}Mo solution, could exist as anionic carbonate complexes. When the solution is acidified with nitric acid for analysis, any carbonate complexes will be destroyed and the uranium and plutonium will revert to cations.

Because plutonium can exist in any of several oxidation states in the same solution, the analyte plutonium (^{239}Pu) and the tracer (^{242}Pu) can be in different oxidation states and behave differently chemically. Many published analytical separations for plutonium require that the plutonium be in a particular oxidation state. The method described here has the advantage that it is not sensitive to the oxidation state of the plutonium.

4.0 Measurement of the Actinides

The most straightforward way to measure the alpha emitting actinides is by direct counting on an alpha spectrometer. The filter cake of $\text{Gd}(\text{OH})_3$ on the surface of a membrane filter makes a good counting mount for alpha spectrometry. The method is very simple, and the spectral resolution is adequate to resolve ^{242}Pu from ^{239}Pu .

Uranium and plutonium could be measured with very high sensitivity by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The $\text{Gd}(\text{OH})_3$ precipitate can be easily dissolved in dilute nitric acid for analysis by ICP-MS.

5.0 Analytical Method

5.1 The sample

The analytical sample is assumed to be a dilution of the ^{99}Mo solution, about 10 mCi/mL before decay, made up in 0.20M NaOH, 0.010M Na_2MoO_4 , and 0.010M NaNO_3 . The sample will have high beta-gamma activity.

5.2 Precautions

The analytical sample has high beta-gamma activity and must be handled with extension tools and stored behind shielding. The sample vial should not be opened by direct handling; a jig should be used to remove the cap. Most of the beta-gamma activity will be found in the filtrate after the first filtration. The filtrate should be kept behind shielding to minimize exposure to laboratory staff.

The sample is made up in 0.20M sodium hydroxide, which is corrosive to skin and eyes. The sample is acidified with dilute nitric acid, which poses a minor risk to skin and eyes. The procedure uses concentrated ammonium hydroxide, a moderately strong base, which is corrosive to skin and eyes. The entire operation should be carried out in a fume hood.

5.3 Quality Control

The sample is measured with an automatic pipet. The volume delivered by the pipet should be checked by pipetting water into a cup and weighing the water delivered, using a balance that shows four places past the decimal. Weigh several pipettings, and then calculate the average volume delivered and the standard deviation. The balance should be checked before use by weighing a check weight.

Actinide analysis by alpha spectrometry typically uses tracers. A tracer causes the counting efficiency to algebraically drop out of the calculations. The tracer must have an accurately known concentration and must be traceable to some accepted standard, such as NIST. The tracer level should be chosen so that the counting error in the tracer peak is too small to control the overall uncertainty. A typical tracer level for low-level counting is 5 to 10 decays per minute. The tracer recovery by this method should be very high, in the range of 80% to 100% in each precipitation. A low tracer recovery will cause the analytical data to have high uncertainty.

Uranium is typically traced with ^{232}U , plutonium with ^{242}Pu , and americium with ^{243}Am . Each tracer should be used to measure only its element. The ^{232}U tracer has a short-lived decay chain that ingrows to measurable levels within a period of months. The ^{232}U decay chain will cause alpha peaks to appear in the alpha spectrum and can interfere with measurement of plutonium and americium. Plutonium-242 will

not bother uranium or americium measurements, but the ^{243}Am peak is very close to the ^{239}Pu analyte peak and will cause an artificially high count rate for ^{239}Pu .

This procedure can be run without tracers. The procedure and the analyst must be known to get high chemical recovery (from spike results).

Prepare a simulant solution with the composition of the samples, but with no ^{99}Mo . Use this solution for making reagent spikes and reagent blanks. Prepare at least one reagent spike and one reagent blank with the analytical batch. The spike level is usually chosen to be close to the reporting limit, or five to ten times the detection limit. If sample volume permits, prepare a duplicate sample. The quality program may require that a sample be spiked with a known amount of an analyte, and then run as a sample (a matrix spike).

The spike results should average 100% over the long term. The standard deviation of the spike results should agree with the calculated uncertainty. The blanks should have negligible activity, since the general work area will not be contaminated with actinides.

The counting instrumentation will have quality requirements independently of this procedure. The counting instrumentation will have a current energy calibration, current efficiency calibration, recent counting chamber background, and a recent pulser check. (Check sources are normally not routinely counted on alpha spectrometers, since counting is done under a vacuum and the check source will slowly sputter contamination on the detector.)

The spectral resolution must allow clean separation of the peaks, or the data will be biased. If one alpha peak sits on the tail of another, then the lower energy peak will have a high bias and the higher energy peak will have a low bias. Americium-243 and -241 are particularly prone to this, since they are very close together. Americium spectra can be mathematically deconvoluted by forcing the high energy peak tail to take the shape of the low energy peak, then subtracting one peak from the other.

5.4 Reagents and Equipment

- Filtration apparatus, for 2.5-cm filter, mounted above a side-arm flask, attached to a vacuum supply
- Stainless steel counting disks (to fit the alpha spectrometers)
- Cardboard holders for transporting and storing counting disks
- Double-sticky tape
- 15-mL centrifuge tubes (such as Corning disposable polyethylene tubes). Need 2 for each sample, including spikes, duplicates, and blanks.
- 2.5-cm membrane filters, 0.1 or 0.2 μm , resistant to strong bases (polyethylene, polypropylene, polysulfone). This procedure has been tested with Pall Metrical polypropylene filters, 0.1 μm pore size, part number M5PU025.
- Filter separators, to go under the membrane filter on the filtration apparatus and prevent cross-contamination from one sample to the next. This procedure has been tested with Pall polypropylene separators, 25 mm diameter, part number 61756.

- Disposable plastic transfer pipets (draws approximately 2.5 mL with one squeeze of the bulb)
- Disposable plastic beakers, around 20-30 mL size. Need 1 for each sample.
- 0.1M nitric acid (add 0.637 mL of commercial concentrated nitric acid (15.7M) to 100 mL of deionized water)
- Gadolinium carrier, 1000 µg/mL in dilute nitric acid (commercially available)
- Concentrated ammonium hydroxide
- 1M ammonium hydroxide (dilute concentrated ammonium hydroxide 1:15 with water)
- Dry, absolute ethanol (NOT denatured alcohol)
- Fine-tip tweezers suitable for picking up a membrane filter
- Pipet and tips, for measuring the ⁹⁹Mo sample, tracers, and spikes (typically 1 mL, 0.5 mL, 0.1 mL, and 0.05 mL)
- Four-place laboratory balance, for measuring volume delivered by the pipets

5.5 Procedure

This procedure is designed to handle a sample up to about 1 mL. If the sample size is increased beyond 1 mL, the volume of nitric acid in step 8 will need to be increased. Enough nitric acid must be used to acidify the sample.

This procedure is written to mount the samples manually, using a single filter holder. A vacuum manifold could be used instead, with several filter holders in parallel. If a vacuum manifold is used, then the mechanical details will change slightly.

The analytical batch will include a blank, at least one spike, and possibly a duplicate sample. All of these are considered samples in the procedure that follows, and all are to be treated identically.

Initial Preparations

1. Assemble the vacuum filtration apparatus.
2. Clean a stainless steel counting disk for each sample, including duplicates, spikes, and a blank.
3. Label each disk with its sample number.
4. Label cardboard holders for the counting disks.
5. Place double-sticky tape on each counting disk, with the label on the back side. Put the counting disk, with tape, in its cardboard holder. Set the cardboard holders on a clean tissue in the work area. (Do not close the cardboard holders, or the cardboard lid will stick to the tape.)

6. Label two sets of centrifuge tubes with the sample numbers. Label one set sample nn-A and the other set sample nn-B. (One set of tubes will be used for the first precipitation, and the second set will be used for the second precipitation.)
7. Label a disposable plastic beaker for each sample, including duplicates, spikes, and the blank.

First Precipitation

8. Set up the sample A centrifuge tubes in order. To each tube, add 3 mL of 0.1M nitric acid. The nitric acid will neutralize the sample and leave it slightly acidic.
9. To each centrifuge tube, add 0.050 mL of gadolinium carrier (50 μg of gadolinium).
10. Add tracers as required (typically, ^{232}U , ^{242}Pu , or ^{243}Am). If tracers are used, then every sample will get the tracers, including spikes and blanks.
11. Add spikes as required (typically, ^{235}U , ^{239}Pu , ^{241}Am). Add spikes ONLY to samples intended to get the spike!
12. Measure each sample into its centrifuge tube. A typical sample size is 1 mL.
13. To each centrifuge tube, add 1 mL of concentrated ammonium hydroxide. This volume is not critical. Ammonium hydroxide is best measured with a plastic transfer pipet; it is difficult to measure with an automatic pipet.
14. Gently mix each centrifuge tube.
15. Allow the tubes to stand for approximately 20 minutes for the $\text{Gd}(\text{OH})_3$ precipitate to complete form.
16. Place a clean filter backer and membrane filter on the filtration apparatus. Turn on the vacuum supply to keep the filter and backer in place.
17. Put several drops of dry absolute ethanol on the filter. Before the ethanol dries, pass the first sample through the filter.
18. Rinse the centrifuge tube thoroughly with 2.5 mL of 1M ammonium hydroxide, then pass the rinse through the filter. (The rinse volume is not critical.) Rinse the tube a second time the same way. Always allow each rinse to completely pass through the filter before adding the next. Discard the centrifuge tube after the second rinse.

19. Add 2.5 mL of deionized water directly to the filter and allow it to pass through. (The rinse volume is not critical.) After it has passed through the filter, add a second rinse of 2.5 mL of deionized water and allow it to pass through.
20. Use tweezers to retrieve the filter from the filter apparatus. Get only the filter, not the backer. Handle the filter by the edge, where there is no $\text{Gd}(\text{OH})_3$ precipitate.
21. Place the filter in its disposable beaker.
22. Remove the used backer from the filtration apparatus and discard it. Place a clean backer and filter on the filtration apparatus.
23. Mount the remaining samples the same way. Put each filter into its disposable beaker.

Second Precipitation

24. After all the samples have been precipitated and filtered and all the filters are in their disposable beakers, adjust the work area as necessary to eliminate the high dose rate from the samples collected in the side-arm flask.
25. To the first sample filter in its plastic beaker, add 1 mL of 0.1M nitric acid. Use a plastic transfer pipet to wash the nitric acid over the surface of the filter to dissolve the $\text{Gd}(\text{OH})_3$ precipitate, then move the solution to the corresponding centrifuge tube (the B tube).
26. Rinse the filter again the same way, using 1 mL of 0.1M nitric acid as before. Wash it over the surface of the filter as before, and transfer the rinse to its centrifuge tube.
27. Rinse the filter a third time the same way. Transfer the rinse to the centrifuge tube. At this point, the centrifuge tube will have 3 mL of 0.1M nitric acid, with the dissolved $\text{Gd}(\text{OH})_3$ precipitate.
28. Dissolve the precipitates off the other filters the same way.
29. To each tube, add 1 mL of concentrated ammonium hydroxide as before. Mix the contents of each tube, and then let the tubes stand for 20 minutes for the precipitates to completely form.
30. Mount the first sample precipitate onto a filter, as before. Rinse it exactly as before: Twice with 2.5 mL of 1M ammonium hydroxide, then twice with water.
31. Place the filter (which is probably still wet) directly in the center of the counting disk. Tap it down onto the tape in several places with the edge of the tweezer. Immediately wipe off the tip of the tweezer with a clean tissue.
32. Mount the remaining samples the same way.

33. After all of the samples have been mounted on filters for counting, allow the filters to dry completely in the fume hood (10 to 20 minutes). When the filters appear dry, they are dry enough. (Any water left in the samples will immediately dry in the vacuum of the alpha spectrometer and will do no harm.)
34. Remove the sample mounts from the hood and take them to the alpha spectrometer.
35. Count the samples as usual.
36. Empty the side-arm flask into a waste container. Rinse out the side-arm flask with water and allow it to dry. Clean up the work area and leave it ready for the next batch of samples.

6.0 Calculations

After the samples have been counted, evaluate the alpha spectra. It is good practice to check the integration of each alpha peak and adjust as necessary, rather than accepting the software's peak area. Results, uncertainty, and detection limit will be calculated automatically, such as in a Microsoft Excel spreadsheet. It is necessary only to key in the counting data. Results can be calculated manually as follows:

$$\text{Activity} = (\text{tracer activity}) \frac{(\text{analyte net peak area})}{(\text{tracer peak area})(\text{sample size})}$$

$$1s \text{ counting error} = (\text{tracer activity}) \frac{\sqrt{\text{analyte net peak area} + 2 \times \text{background}}}{(\text{tracer peak area})(\text{sample size})}$$

The calculated units will be the same units the tracer activity is given in.

The total uncertainty will normally be heavily dominated by counting error, since the expected alpha activity in ⁹⁹Mo solution is low. The other sources of analytical uncertainty are small compared to counting error at low analyte activity. Calculate the total propagated uncertainty as the quadratic sum of the component uncertainties. That is, express each uncertainty as a fraction, square each fractional uncertainty, add all the squares together, then take the square root of the sum. The result will be total propagated uncertainty expressed as a fraction.

$$\text{Total propagated uncertainty} = \sqrt{x_1^2 + x_2^2 + \dots x_n^2}$$

x_1 is counting error, which may be very large at low activity

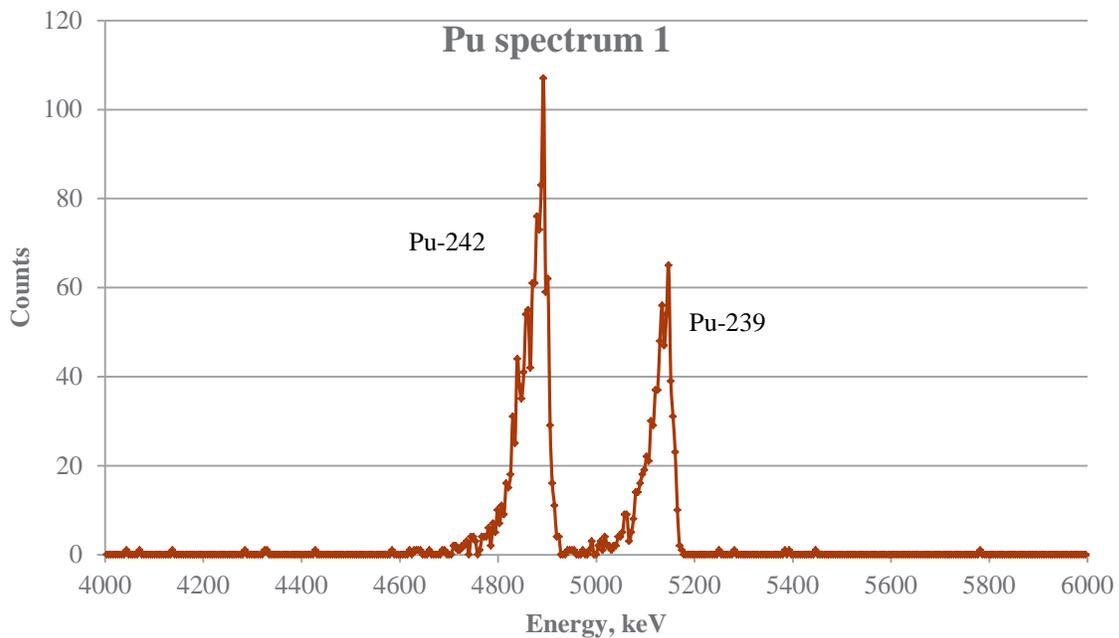
x_2 is pipetting error, typically 2% or less

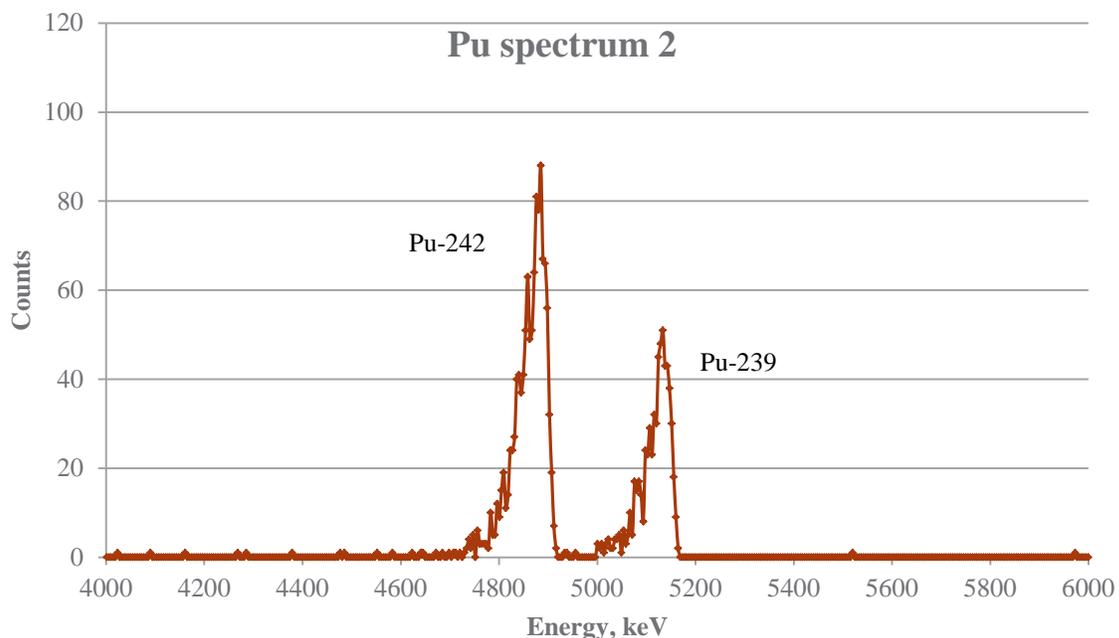
x_3 is uncertainty in the tracer activity, typically a few percent

Include any other sources of uncertainty as appropriate. (If the analytical result is zero, then the counting error cannot be expressed as a fraction, and the total propagated uncertainty must be calculated as activity, not a fraction. When the analytical result is zero, counting error is the only significant source of uncertainty and can be reported as total uncertainty.)

7.0 Typical Alpha Spectra

This method gives alpha spectral resolution adequate to cleanly separate ^{239}Pu from ^{242}Pu . Two typical spectra generated using this method are shown below.





These two spectra were generated by spiking a simulated ^{99}Mo solution with ^{239}Pu . The simulant was chemically identical to the pharmaceutical ^{99}Mo solution, but did not have actual ^{99}Mo (0.200M NaOH, 0.010M Na_2MoO_4 , 0.010M NaNO_3).

Sample size	1 mL (simulated ^{99}Mo solution)
Membrane filter	Pall brand Metrice polypropylene, 0.1 μm pore size
Pu-242 tracer activity	8.80 dpm (0.148 Bq)
Pu-239 spike activity	5.50 dpm (0.092 Bq)
Count length	960 minutes
Detector counting efficiency	0.204 counts per decay

These two spectra were generated using a double precipitation, exactly as described in the method above. The tracer yield in each spectrum is about 67%. At this tracer yield, spike level, and count length, the counting error in the ^{239}Pu result is about 4% at one standard deviation. At 95% confidence (2 standard deviations), the spread of the data should be about $\pm 10\%$ (including the uncertainty of the tracer and the pipets, which are 2-3 percent). These two spike recoveries are 107% and 95%, which are well within the expected spread of $\pm 10\%$.

8.0 References

¹ Lloyd A. Currie, Limits for Qualitative Detection and Quantitative Determination, *Analytical Chemistry*, vol 40, no 3 (1968) pp 586-593

² Cleveland, J. M., *The Chemistry of Plutonium*. Gordon and Breach, New York, 1970.

³ Schultz, *The Chemistry of Americium*, Technical Information Center, Energy Research and Development Administration, 1976. See chapter 3.

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